

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
16 May 2002 (16.05.2002)

PCT

(10) International Publication Number  
**WO 02/38630 A1**

(51) International Patent Classification<sup>7</sup>: **C08F 10/08**,  
10/10, 110/08

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(21) International Application Number: PCT/KR01/01901

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(22) International Filing Date:  
9 November 2001 (09.11.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
2000/67057 13 November 2000 (13.11.2000) KR

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK,  
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK,  
SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,  
ZW.

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(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG).

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**Published:**

- with international search report
- entirely in electronic form (except for this front page) and  
available upon request from the International Bureau

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

**Best Available Copy**

(54) Title: METHOD FOR PRODUCING POLYBUTENE

(57) Abstract: The present invention provides a method for producing high reactive polybutene (HRPB) in which carbon-carbon double bond is positioned at an end of polybutene. The method produces polybutene having 300-5000 of number average molecular weight (Mn) from (a) isobutene, (b) C4 hydrocarbon compounds derived from cracking of naphtha, and containing more than 10 weight% of isobutene, and (c) C4 hydrocarbon compounds derived from a refining process of crude oil or from catalytic cracking of heavy gas oil, and containing more than 10 weight% of isobutene by using catalyst comprising secondary alkylether, tertiary alcohol, and boron trifluoride.

WO 02/38630 A1

## METHOD FOR PRODUCING POLYBUTENE

### BACKGROUND OF THE INVENTION

#### 5 (a) Field of the Invention

The present invention relates to a method for producing polybutene and, more particularly, to a method for producing high reactive polybutene (HRPB) in which carbon-carbon double bond is generally positioned at the end of the polybutene.

#### 10 (b) Description of the Related Art

Polybutene is generally produced by polymerizing C4 olefin including isobutene using Friedel-Craft type catalyst and has about 300~5000 of number average molecular weight Mn. Remains after extracting 1,3-butadiene from C4 olefin is C4 raffinate-1, and the C4 raffinate-1 comprises paraffin such as  
15 iso-butane and normal-butane and olefin such as 1-butene, 2-butene, and isobutene. Here, the isobutene content is generally about 30~50weight%. The C4 raffinate-1 is generally used for producing methyl-t-butylether (MTBE) which is used as an octane number improver, or polybutene. The produced polybutene is mainly composed of isobutene units since the isobutene has the highest reactivity  
20 among olefins in the C4 raffinate-1. Polybutene may also be produced from butane-butene oil (B-B oil) which is a C4 mixture derived from crude oil refining process, or can be produced from high purity isobutene.

The viscosity of polybutene increases as its molecular weight increases and the viscosity is about 4~40000cSt(centi-stocks) at 100°C. In addition,

polybutene is pyrolyzed at a temperature of more than 275°C without leaving residue, and has high solubility in lubricant or fuel because of its branched alkyl structure. For these reasons, polybutene is used as an anti-scuff agent or a viscosity index improver in engine oil, or used as detergent by being mixed with  
5 fuel of internal-combustion engine such as a vehicle.

Contrary to the past when high reactive polybutene is not preferred since the same is mainly used for adhesive or insulating oil, the demand for high reactive polybutene constantly increases. This is due to the fact that the use of high reactive polybutene having a polar group as fuel detergent or lubricant additive  
10 gradually increases.

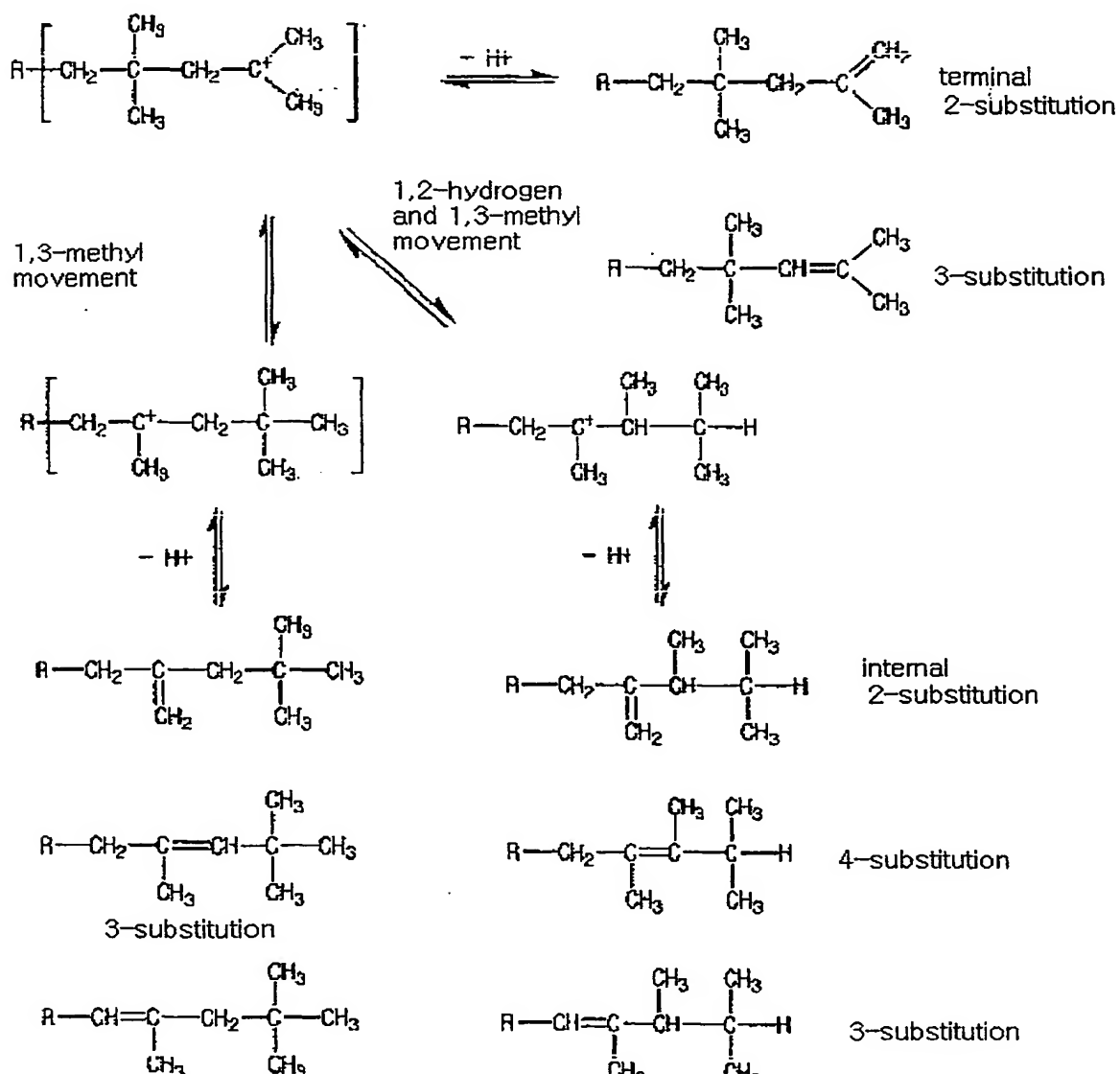
The most widely used polybutene formed by introducing a polar group is polyisobutenyl succinic anhydride (PIBSA) manufactured by reacting polybutene with maleic anhydride. Most of lubricant additive or fuel detergent is manufactured with PIBSA as intermediate. In case that the double bond of  
15 polybutene is positioned at its end, high yield of PIBSA is obtained, however, when the double bond is positioned further towards the interior of the polybutene and the number of alkyl group substituted to the double bond increases, reactivity of polybutene is lowered, which decreases the PIBSA yield.

For increasing reactivity of polybutene, a method of chlorinating polybutene  
20 with chlorine gas and then, reacting the chlorine product with maleic anhydride is known. However, this method is not preferable in an economic and an environmental aspect since it costs much due to the expensive equipment for preventing corrosion of reactor, and a large quantity of base solution should be used to neutralize unreacted chlorine gas. In addition, when PIBSA containing  
25 increased amount of chlorine is used for fuel additives, it may cause corrosion of

engine.

Accordingly, researches for increasing reactivity of polybutene by changing its polymerization condition are constantly in progress. Types of double bond that effects reactivity of polybutene are variable according to the number of alkyl group substituted in its double bond as shown in equation 1.

[ Equation 1 ]



As Friedel-Craft type catalyst for producing polybutene, aluminum trichloride or boron trifluoride are generally used, and high reactive polybutene that contains relatively high content of terminal double bond is obtained when boron trifluoride is used. For example, it is reported in Journal of Polymer Science, Symposium no. 56, 191-202(1976), that content of terminal double bond increased up to 40% for 5~7 minutes of contact time when boron trifluoride or complex compound of boron trifluoride are used with co-catalyst such as acetic acid or water. According to this method, polybutene which contains remarkably high content of terminal double bond can be obtained while the content of terminal double bond is 5~20% when conventional aluminum trichloride is used.

However, there is also disclosed that as the contact time is longer, the position of the vinylidene (terminal double bond) of polymer is moved to the internal position of the polymer, and therefore, polybutene tends to change into low reactive one. This is indirectly verified in Khim i Teknol, Toplivi masel, vol. 10, pp 23-26, written by Mullin M. A. According to this literature, methanol or mixture of methanol/ethanol and complex compound of  $\text{BF}_3$  are used and the contact time is maintained to 30~40 seconds. This means that there must be paid careful attention to use this type of catalyst.

The fact that the contact time should be maintained to be short when boron trifluoride catalyst is used for isobutene polymerization is also emphasized in European Patent No. 016312 A1. There is disclosed that the contact time and the concentration of catalyst should strictly be controlled, and especially, the contact time should be maintained within 40 seconds to prevent double bond isomerization.

In European Patent No. 400,905 A1, there is disclosed that when boron

trifluoride which forms complex with ethanol is used, the contact time can be extended to more than 1 minutes, possibly 8~70 minutes, and more preferably 12~20 minutes almost without isomerization of double bond in a product, and therefore, reaction variables can effectively controlled. The invention of this patent is regarded as an advanced one because the product can maintain the content of vinylidene of more than 70% while maintaining the contact time of more than 8 minutes.

In U.S. Patent No. 5,688,887, there is disclosed a method for producing polybutene having more than 80% of vinylidene by using boron trifluoride- ether having at least one tertiary alkyl complex, and this method has an advantage that small isomerization is happened even though the contact time is maintained long. The reason why small isomerization is happened even though the contact time is maintained long is that the used catalyst does not induce initiation reaction by proton. That is, the catalyst does not to provide proton, and thus prevents proton from lowering the content of vinylidene by isomerization. According to an embodiment of the above-mentioned patent, the most desirable result is obtained when ether having both the secondary alkyl and the tertiary alkyl (for example, isopropyl t-butylether) is used. However, the above-mentioned ether compound is a material not commercialized, so, to use the material as co-catalyst (initiator), an additional equipment to produce the compound is required. For this reason, the above-mentioned method is supposed not to be commercially generalized.

In U.S. Patent No. 5,408,018, there is disclosed a method for producing polybutene containing more than 80% of vinylidene and narrow molecular weight distribution by using secondary alcohol - boron trifluoride complex as catalyst. However, the invention of this patent has disadvantages in that the reaction

condition, such as reaction temperature, is difficult to control since the reaction temperature is relatively low, and the contact time should be controlled within 9 minutes.

5

### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method of producing high reactive polybutene containing more than 80% of terminal double bond. Further, the present invention is to provide a method of producing high reactive polybutene in which the content of terminal double bond changes a little even  
10 though the contact time is prolonged.

It is another object of the present invention to provide new catalyst for producing high reactive polybutene which is easy to purchase and inexpensive, and allows polybutene to contain high content of terminal double bond even though the contact time is prolonged.

15

To achieve the above objects, the present invention provides a method of producing polybutene having 300~5000 of number average molecular weight (Mn) from (a) isobutene, (b) C4 hydrocarbon compounds derived from cracking of naphtha, and containing more than 10 weight% of isobutene, or (c) C4 hydrocarbon compounds derived from a refining process of crude oil or from  
20 catalytic cracking of heavy gas oil, and containing more than 10 weight% of isobutene, with using catalyst comprising secondary alkylether, tertiary alcohol, and boron trifluoride. Here, it is preferable that the amount of boron trifluoride catalyst is 0.05~1.0 weight part per 100 weight part of isobutene in hydrocarbon compounds, the mole ratio of co-catalyst formed of secondary alkylether and  
25 tertiary alcohol : boron trifluoride is 1.0~2.0 : 1 and more preferably, the mole ratio

of secondary alkylether : tertiary alcohol is 0.5~1.2:1.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The detailed description of the present invention is provided hereinafter.

5       The present invention is characterized in that catalyst formed of secondary alkylether, tertiary alcohol, and boron trifluoride is used to produce polybutene in which the content of terminal double bond to entire double bond is more than 80%. In any conventional method of producing polybutene, tertiary alcohol is not used as co-catalyst. That is because the content of vinylidene is lowered when tertiary  
10   alcohol is used compared with cases when secondary or primary alcohol is used. However, the inventors of the present invention discovered a fact that when tertiary alcohol is used with secondary alkylether, the content of terminal double bond of polybutene increases and is not influenced much by the contact time.

      Secondary alkylether used for the present invention is symmetrical or  
15   asymmetrical secondary alkyl ether having alkyl group of carbon number of 3~20, preferably, selected from the group consisting of diisopropylether, di(sec-butyl)ether, di(sec-hexyl)ether, di(sec-octyl)ether and mixtures thereof, and more preferably diisopropylether. For example, polybutene which has high content of vinylidene and is not influenced much by contact time in polymerization  
20   reaction can be produced by using catalyst obtained as follows: boron trifluoride is added to diisopropylether to form solid complex and then, tertiary alcohol, such as t-butylalcohol (TBA), is added to the solid complex to form liquid catalyst.

      Tertiary alcohol used for the present invention is tertiary alcohol having carbon number of 4~20, preferably, selected from the group consisting of



t-butylalcohol, diacetonalcohol (4-hydroxy-4-methyl-2-pentanone), 2-methyl-2-butanol and mixtures thereof, and more preferably, t-butylalcohol or 2-methyl-2-butanol. Diisopropylether as secondary alkylether and t-butylalcohol as tertiary alcohol is easy to purchase, therefore additional equipment for producing diisopropylether or t-butylalcohol is not required.

To produce catalyst by reacting secondary alkylether, tertiary alcohol, and boron trifluoride with each other, it is preferable to add boron trifluoride to secondary alkylether or mixed solution of secondary alkylether and tertiary alcohol. If boron trifluoride is added to tertiary alcohol without secondary alkylether, catalyst turns into black material and there is possibility to obtain polybutene having low content of vinylidene. When boron trifluoride is added to secondary alkylether, for example, diisopropylether, solid material is formed by reaction of boron trifluoride and secondary alkylether. Then, tertiary alcohol, for example, t-butylalcohol is added to dissolve the solid material, so that the dissolved material is used as catalyst. Considering efficiency of catalyst manufacturing process, it is preferable to add boron trifluoride to mixture of secondary alkylether and tertiary alcohol. It is experimentally verified that the properties of catalyst are not influenced in this case.

Since the reaction for forming complex of boron trifluoride and co-catalyst is exothermic reaction, it is preferable to remove heat of reaction for preventing the decomposition of catalyst and run-away reaction. Accordingly, it is preferable that the catalyst manufacturing reaction is performed at a temperature of lower than 40°C, preferably lower than 20°C, and more preferably -40°C~0°C at which the stability of catalyst can maintain because the heat of reaction is satisfactorily

removed.

The amount of catalyst component,  $\text{BF}_3$  is preferably 0.05~1.0 weight part per 100 weight part of isobutene in raw material (hydrocarbon compounds), and polybutene produced according to the present invention generally has 300~5000 of number average molecular weight ( $M_n$ ). When the amount of  $\text{BF}_3$  is more than 1.0 weight part, the polymerization process becomes non-economical, and catalyst should be removed from product by additional process. When the amount of  $\text{BF}_3$  is less than 0.05 weight part, there is problem that the yield of polybutene becomes lower.

It is preferable that the mole ratio of secondary alkylether/tertiary alcohol used for the present invention is 0.5~1.2. It is more preferable that the amount of tertiary alcohol does not exceed the amount of secondary alkylether, that is, the more preferable mole ratio of secondary alkylether/tertiary alcohol is 1.0~1.2. If the amount of tertiary alcohol increases, the amount of boron trifluoride should increase to maintain activity of catalyst. In this case, there is possibility that catalyst is degraded. The mole ratio of co-catalyst formed of secondary alkylether and tertiary alcohol to boron trifluoride is preferably 1.0~2.0:1, and more preferably 1.2~1.8:1 in an aspect of catalyst activity. When the mole ratio of co-catalyst/boron trifluoride is over 2.0, the activity of catalyst is lowered to remarkably reduce the yield of polybutene, and when the mole ratio thereof is less than 1.0, the content of vinylidene is considerably lowered.

When necessary, polar solvent may additionally be used to disperse the

catalyst in the raw material. As the polar solvent, more than one compound selected from the group consisting of chloromethane, dichloromethane, and chloroform can be used, and it is preferable to use more than 50 weight part of the polar solvent per 100 weight part of the catalyst and co-catalyst.

5

The catalyst can be added to the polymerization reaction in various ways. For example, the catalyst of the present invention can be separately formed, and then the obtained liquid catalyst can be added into a polymerization reactor. In addition, the raw material (hydrocarbon) of polybutene, co-catalyst, and catalyst  
10 can be put into the reactor at the same time through separately formed supply lines. In the other way, the co-catalyst and the raw material of polybutene are mixed, and the mixed material is put into the reactor, and then gaseous boron trifluoride catalyst is supplied into the reactor through another supply line. In all cases, the amount of catalyst, the mole ratio of catalyst and co-catalyst and the mole ratio of  
15 co-catalysts should be maintained as described above.

In U.S. Patent No. 5,191,044, there is disclosed that polybutene having high content of vinylidene can be produced when free  $\text{BF}_3$  is removed from the polymerization reactor by using vacuum or passing inert gas through the reactor.  
20 However, in the present invention, the free  $\text{BF}_3$  does not influence much on the vinylidene content. Thus, the additional  $\text{BF}_3$  removing process is not required in the present invention, and the catalyst of the present invention is superior to conventional catalyst in an economical aspect.

25

Examples of raw material for producing polybutene of the present invention

includes (a) isobutene, (b) C4 hydrocarbon compounds (for example C4 raffinate) derived from cracking of naphtha, and containing more than 10 weight% of isobutene, and (c) C4 hydrocarbon compounds (for example, B-B oil) derived from a refining process of crude oil or from catalytic cracking of heavy gas oil, and  
5 containing more than 10 weight% of isobutene.

When isobutene, especially isobutene having high purity or isobutene diluted with a saturated hydrocarbon is used, there is a defect that the price of raw material increase, but the un-reacted raw material can be recovered from the  
10 reactor and re-used. In the cation polymerization reaction, the lower the reaction temperature is and the lower the conversion ratio of the raw material into resin is, the larger the molecular weight is. When it is difficult to maintain the reaction temperature low enough, it is possible to increase the molecular weight by lowering the resin conversion ratio. However, if the material is not pure, the raw  
15 material composition continuously changes when the same is re-used, so, it is impossible to manufacture the product having uniform quality.

Since B-B oil or C4 raffinate comprises normal butene such as 1-butene and 2-butene as well as isobutene and is outstandingly low in price in comparison  
20 with that of pure isobutene, the same is generally used as raw material for producing polybutene. This normal butene has low reactivity in comparison with that of isobutene, but has ordinary reactivity, so a part thereof is converted into resin. When the reaction temperature increases, the more normal butene participates in the polymerization reaction. Then the viscosity of polybutene  
25 becomes high, and thermal stability thereof is lowered in comparison with that of

polybutene not including normal butene. Accordingly, when raw material including normal butene is used, it is required to maintain the temperature of polymerization reaction properly. Generally, the preferable temperature is  $-50^{\circ}\text{C}\sim 20^{\circ}\text{C}$ , more preferably  $-40^{\circ}\text{C}\sim 10^{\circ}\text{C}$ , and most preferably,  $-30^{\circ}\text{C}\sim 0^{\circ}\text{C}$ .

- 5 When the reaction temperature is more than  $20^{\circ}\text{C}$ , the participation ratio of normal butene increases though the conversion ratio is maintained low. When the reaction temperature is less than  $-50^{\circ}\text{C}$ , the reactivity is excessively lowered, which results in lower productivity and the excessively high molecular weight. In this case, it is difficult to use polybutene as fuel detergent or lubricant additive.

10

- The reaction pressure should be set for the raw material to be maintained in a liquid state at the reaction temperature, and the preferable reaction pressure is more than  $3\text{kg}/\text{cm}^2$ . The contact time, meaning the time for which the raw material is in the polymerization condition in a continuous polymerization reaction,
- 15 is closely related with the conversion ratio. The contact time should be set in consideration of an aspect of economical use of raw material and the participation ratio of normal butene. Generally, the preferable conversion ratio of isobutene is more than 50%, more preferably 70~99%, and most preferably 80~95%. When catalyst of the present invention is used, the contact time required to obtain such a
- 20 conversion ratio is approximately 5~180 minutes though the contact time can be varied according to the reaction temperature and the amount of catalyst. When the reaction temperature is lowered, the reaction speed is slow; accordingly, it is required to extend the contact time to obtain the desired conversion ratio.

Preferred examples of the present invention and comparative examples are provided hereinafter. However, the present invention should not be understood to be restricted to the examples described below.

5 [Example 1]

3.63g(54mmol) of gaseous boron trifluoride was introduced into 100ml reactor in which 7.65g(75mmol) of diisopropylether (IPE) was contained while cooling the reactor to -5°C and stirring the reactor. 5.4g(75mmol) of t-butylalcohol was added to the produced white crystal and stirred for 5 minutes to completely  
10 dissolve the white crystal. After passing nitrogen through the reactor for 5 minutes, the final catalyst was obtained. The obtained catalyst and raw material (C4 raffinate-1) having composition as shown in table 1 were continuously introduced into a pressure reactor, which was maintained to -6°C by a cooler. The pressure of reactor was maintained to more than 3kg/cm<sup>2</sup> so that the raw  
15 material was in the liquid state. Average contact time was maintained to 45 minutes, and the catalyst was introduced so that 0.2 weight part of BF<sub>3</sub> was introduced per 100 weight part of the isobutene.

[Table 1]

Component	isobutane	n-butane	1-butene	C-2-butene	T-2-butene	i-butene
Content (weight%)	2.09	6.79	29.71	4.41	9.50	47.51

20 180 minutes after, polymerization was stopped by directly introducing the polymerization product into a receptacle in which excess methanol was contained from the outlet of the reactor. The polymerization product was diluted with hexane, the volume of which was 3 times of the polymerization product, and

washed 3 times with water, and then solvent was removed. Finally, oligomer was removed by stripping the polymerization product at the condition of 220°C, 5mmHg for 30 minutes. The molecular weight of the obtained polybutene was measured by GPC and the content of vinylidene was analyzed by C13-NMR. As a result, the conversion ratio of isobutene was 99%, the molecular weight ( $M_n$ ) was 1030, the polydispersity(Pd) was 1.52, and the content of vinylidene was 86%.

### [Example 2]

17.68g(261mmol) of gaseous boron trifluoride was introduced into 100ml reactor in which 19.13g(188mmol) of diisopropylether and 13.12g(177mmol) of t-butylalcohol were contained while cooling the reactor to -5°C and stirring the reactant to obtain the catalyst. Polybutene was produced in the same way as that of example 1, except that the polymerization temperature and the contact time were set according to table 2. Catalyst was used after removing free  $BF_3$  by passing nitrogen through the catalyst for 5 minutes except the one marked "Free  $BF_3$  not removed" in table 2.

[Table 2]

Reaction temperature(°C)	Contact time (minute)	Conversion ratio (%)	Molecular weight $M_n$ (polydispersity)	Vinylidene (%)
-4 (Free $BF_3$ not removed)	45	99	180 (1.30)	82
-4	45	98	830 (1.36)	83
-6	45	95	920 (1.45)	85
-8	15	82	1400 (1.80)	87
-9	45	87	1420 (1.90)	89
-12	45	75	1750 (2.05)	92

15

-12	90	90	1680 (1.95)	90
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### [Example 3]

Catalyst, which was produced in example 2, and in which free  $\text{BF}_3$  was removed, was used, and the raw material including 65weight% of isobutene and 35weight% of isobutane was used. The polymerization was performed at  $-12^\circ\text{C}$  of reaction temperature and for 45 minutes of contact time. After-treatment was performed in the same way as described in example 1, and properties of resin was analyzed. As a result, the molecular weight ( $M_n$ ) was 1850, the polydispersity( $P_d$ ) was 1.85, the content of vinylidene was 93%, and the conversion ratio of isobutene was 82%.

### [Example 4]

2.62g(25.6mmol) of diisopropylether and 1.90g(25.6mmol) of t-butylalcohol were mixed with 4000ml of C4 raffinate-1 having the composition shown in table 1. The mixed compounds were introduced into a 330ml reactor at  $-16^\circ\text{C}$  and at a speed of 4.03g/minute, and gaseous boron trifluoride was introduced at a speed of 1.5ml/minute at the same time. Average contact time was 45 minutes, and the reaction reaches to normal state 360 minutes after. The molecular weight ( $M_n$ ) was 1970, the polydispersity( $P_d$ ) was 2.15, the content of vinylidene was 87%, and the conversion ratio of isobutene was 90%.

### [Example 5]

Catalyst was produced according to the method in example 1 except that 20g of dichloromethane and 1.1g(15mmol) of t-butylalcohol were used instead of



5.4g of t-butylalcohol. Polymerization was performed in the same way as that of example 1 with using the above-mentioned catalyst. As a result, the conversion ratio of isobutene was 99%, the molecular weight (Mn) was 1040, the polydispersity(Pd) was 1.50, and the content of vinylidene was 84%.

5

[Comparative example 1]

Catalyst was produced according to the method in example 1 except that 20g of dichloromethane was used instead of 5.4g of t-butylalcohol. Polymerization was performed in the same way as that of example 1 with using the  
10 above-mentioned catalyst. As a result, the conversion ratio of isobutene was 99%, the molecular weight (Mn) was 1050, the polydispersity(Pd) was 1.55, and the content of vinylidene was 81%.

[Comparative example 2]

15 Catalyst was produced by adding 16.0g(236mmol) of boron trifluoride to 22.32g(370mmol) of isopropylalcohol (IPA) at -5°C, and then nitrogen was passed through the catalyst for 5 minutes. The raw material of table 1 was used, and the continuous polymerization was performed with using 0.1weight% of catalyst at -8°C for 15 minutes of contact time to obtain polybutene. As a result of analysis  
20 of the obtained polybutene, the conversion ratio of isobutene was 86%, the molecular weight (Mn) of the obtained resin was 1450, the distribution degree was 1.75, and the content of vinylidene was 81%. In case that the contact time was set to 30 minutes in the same condition, the conversion ratio of isobutene was 98%, the molecular weight(Mn) of the obtained resin was 1350, the polydispersity was  
25 1.70, and the content of vinylidene was 73%.

[Comparative example 3]

Catalyst was obtained by cooling 17.82g(202mmol) of methyl-t-butylether, adding 9.79g(144mmol) of boron trifluoride at -5°C, and passing nitrogen through the catalyst for 5 minutes. The continuous polymerization was performed in condition of -8°C of reaction temperature, 15 minutes of contact time, and 0.2weight% of catalyst to obtain polybutene. As a result of analysis of the obtained polybutene, the conversion ratio of isobutene was 84%, the molecular weight (Mn) of the obtained resin was 1300, the polydispersity was 1.82, and the content of vinylidene was 83%.

[Comparative example 4]

Polybutene was produced in the same way as that of comparative example 3 except not performing the step of passing nitrogen to remove free BF<sub>3</sub> after producing catalyst. As a result of analysis of the obtained polybutene, the conversion ratio of isobutene was 86%, the molecular weight (Mn) of the obtained resin was 1250, the polydispersity was 1.92, and the content of vinylidene was 77%.

According to the result of the comparative example 1, in which catalyst produced by using diisopropylether as co-catalyst and dichloromethane as polar solvent was used, the content of vinylidene was lower than that of the examples of the present invention. This shows that the tertiary alcohol is effective as the co-catalyst. From the result of the example 2, when diisopropylether and t-butylalcohol are used as co-catalyst, the molecular weight and the content of

vinylidene increase as the reaction temperature was lowered.

Further, in case of the comparative examples 3 and 4, there was large difference in the content of vinylidene according to the existence of free  $\text{BF}_3$ , while the influence thereof was insignificant in example 2. From the result of example 3,  
5 the content of vinylidene increases as the purity of isobutene increases.

Catalyst used in the present invention has advantages in that the catalyst is easy to commercially obtain, and the after-treatment process is not required. In addition, the catalyst according to the present invention makes it possible to produce polybutene having at least same or considerably high content of  
10 vinylidene in comparison with that of the conventional catalyst.

As described above, according to the present invention, polybutene having high content of vinylidene can be produced by using catalyst formed of secondary alkylether, tertiary alcohol, and boron trifluoride. Further, the catalyst of the present invention is not influenced much by the contact time, and easy to  
15 commercially obtain. In addition, the properties of the produced polybutene do not change much even though free  $\text{BF}_3$  is not removed from the catalyst.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various  
20 modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

**WHAT IS CLAIMED IS:**

1. A method of producing polybutene having 300~5000 of number average molecular weight (Mn) from (a) isobutene, (b) C4 hydrocarbon compounds derived from cracking of naphtha, and containing more than 10 weight% of isobutene, and (c) C4 hydrocarbon compounds derived from a refining process of crude oil or from catalytic cracking of heavy gas oil, and containing more than 10 weight% of isobutene,

characterized in that catalyst comprising secondary alkylether, tertiary alcohol, and boron trifluoride is used.

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2. The method according to claim 1, wherein the secondary alkylether is selected from the group consisting of diisopropylether, di(sec-butyl)ether, di(sec-hexyl)ether, di(sec-octyl)ether and mixtures thereof.

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3. The method according to claim 1, wherein the tertiary alcohol is selected from the group consisting of t-butylalcohol, 4-hydroxy-4-methyl-2-pentanone, 2-methyl-2-butanol and mixtures thereof.

20

4. The method according to claim 1, wherein the polybutene is produced at the temperature of -50~20°C.

5. The method according to claim 1, wherein the amount of the boron trifluoride is 0.05~1.0 weight part per 100 weight part of isobutene in raw material.

25

6. The method according to claim 1, wherein the mole ratio of

co-catalyst including the secondary alkylether and tertiary alcohol : the boron trifluoride is 1.0~2.0:1.

7. The method according to claim 1, wherein the mole ratio of the  
5 seconher/tertiary alcohol is 0.5~1.2.

8. The method according to claim 1, wherein the catalyst further includes one or more solvent selected from the group consisting of chloromethane, dichloromethane, and chloroform.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR01/01901

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7 C08F 10/08, C08F 10/10, C08F 110/08

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08F 10/08, C08F 10/10, C08F 110/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

KOREAN PATENTS AND APPLICATIONS FOR INVENTIONS SINCE 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 322,241 A (EXXON CHEMICAL PATENTS INC.), 28.JUNE.1989 (28.6.1989) SEE ABSTRACT AND CLAIM	1 - 8
Y	WO 200011040 A (NIPPON PETROCHEMICALS COMPANY,LIMITED), 02.MARCH.2000 (02.03.2000) SEE ABSTRACT AND CLAIM	1 - 8
Y	EP 370,805 A (EXXON CHEMICAL PATENTS INC.), 30. MAY.1990 (30.05.1990) SEE ABSTRACT AND CLAIM	1 - 8
A	WO 9940129 A (TARGOR GMBH), 12. AUGUST.1999 (12.8.1999) SEE THE WHOLE DOCUMENT	1 - 8
A	WO 9838225 A (NIPPON PETROCHEMICALS COMPANY,LIMITED), 03.SEPTEMBER.1998 (03.09.1998) SEE THE WHOLE DOCUMENT	1 - 8
A	EP 598,543 A (MITSUBISHI PETROCHEMICAL COMPANY LIMITED), 25.MAY. 1994 (25.05.1994) SEE THE WHOLE DOCUMENT	1 - 8

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

15 FEBRUARY 2002 (15.02.2002)

Date of mailing of the international search report

15 FEBRUARY 2002 (15.02.2002)

Name and mailing address of the ISA/KR

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR01/01901

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